# REVIEW OF ISSUES RELATED TO GULF OF MEXICO HYPOXIA

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#### **ABSTRACT**

Scientific investigations in the Gulf of Mexico have documented a large area of the Louisiana-Texas continental shelf with seasonally-depleted oxygen levels (hypoxia). Nutrient over-enrichment from the Mississippi and Atchafalaya River Basins and stratification in coastal waters are believed to be the major factor contributing to over-production of phytoplankton in the Gulf and the resulting hypoxia. A national Hypoxia Task Force adopted a Hypoxia Action Plan (the Plan) to address this phenomenon. The Region 4 office of the Environmental Protection Agency (EPA) has reviewed previous studies supporting conclusions in the Plan and concludes that additional consideration of the role of phosphorus in hypoxia formation and reduction is warranted.

Region 4 in its review and evaluation of documents and data supporting the development of the Plan reaches the following conclusions:

- 1. The Lower Mississippi and Atchafalaya Rivers deviate from stoichiometric nutrient balance. Dissolved inorganic nitrogen to dissolved inorganic phosphorus (DIN/DIP) ratios greatly exceed the Redfield Ratio and are a factor of 3-4 higher during the high spring river flows when algal production is greatest. Existing data appears to indicate phosphorus is the limiting factor (between nitrogen and phosphorus) in algal production during these periods.
- 2. During the critical late winter and spring months, DIN in the Mississippi River would have to be reduced more than 75% in order to achieve a 16:1 DIN/DIP ratio, and more to achieve DIN limitation. The proposed 30% reduction in Total Nitrogen proposed in the Plan could be expected to have no impact on reducing the hypoxia area.
- 3. Significant data and knowledge gaps exist such that additional data collection, water quality modeling and research are justified. The determination of the ratio of bio-available nutrients especially in the late winter and spring in the Lower Mississippi, Atchafalaya Rivers and northern Gulf of Mexico is a critical need. The EPA Algal Growth Potential Protocol that was published in 1978 could be used to assist in these studies.
- 4. Sources, fate and transport of phosphorus in addition to nitrogen should be evaluated for the Mississippi and Atchafalaya River basins.
- 5. Phosphorus control options should be further considered for effectiveness of control, cost and implementability for Gulf hypoxia.

# TABLE OF CONTENTS

1	INTRODUCTION	5
2	THE EXISTING HYPOXIA ACTION PLAN	5
2	2.1 The Assessment Process	5
_	2.2 Hypoxia Assessment Reports	
	2.2.1 Final Integrated Assessment	
	2.2.2 Simple Box Model of the Louisiana Inner Shelf	
	2.2.3 Hypoxia Action Plan	
2	2.3 EPA Region 4 Review of the Gulf Hypoxia Issue	
3	LOWER MISSISSIPPI AND ATCHAFALAYA RIVERS: NUTRIENT CONCENTRATIONS, NUT	
IVIA	ASS TRANSPORT, AND ELEMENTAL RATIOS	
	3.1 Redfield and Elemental Ratios	
	3.2 Geographic Setting and Monitoring Station Locations	
3	3.3 Lower Mississippi River Nutrient Analyses	10
	3.3.1 Tarbert Landing USGS Gauge (USGS 07373291) Flow Analysis	
	3.3.2 The Luling USGS Station Nutrient Analyses	
	3.3.3 The U.S. Geological Survey (USGS 07373420) St. Francisville Water Quality Monitoring 16	
	3.3.4 The USGS Belle Chasse Water Quality Station Nutrient Analyses	
	3.3.5 Atchafalaya River Nutrient Analyses	22
	DIN and DIP Limiting Concentration and Elemental Ratios in the LMR and ARB	24
3	3.5 Bio-available Nitrogen and Phosphorus	28
4	GULF OF MEXICO PRIMARY PRODUCTIVITY AND HYPOXIA	28
5	ADDITIONAL DATA COLLECTION AND ANALYSIS, ADDITIONAL WATER QUALITY MODELIN	
ΑD	DITIONAL RESEARCH NEEDS	34
5	5.1 Data Collection and Data Analyses	34
	5.1.1 Better Characterization of the Gulf Hypoxia Zone	
	5.1.2 Reevaluation of Nutrient Loads to the Gulf	
5	5.2 Water Quality Modeling Improvement	
	5.2.1 Present Modeling Approach – A Simple Box Model	
	5.2.2 3 Dimensional Hydrodynamic and Water Quality Development	
	5.2.3 Sediment-Water Column Exchange and Regeneration of N and P	
	5.2.4 Impacts of Carbon on the Gulf Sediment Oxygen Demand	
5	5.3 Research Needs	
	5.3.1 Light Limitation	
	5.3.2 Carbon Impacts to Hypoxia	
	5.3.3 Bioavailability Studies on Nutrients	
	5.3.4 Denitrification in the Bottom Waters of the Gulf	
	5.3.5 Role of Nitrogen Fixation by Cyanobacteria in the Gulf	
6	CONCLUSIONS	38
7	BIBLIOGRAPHY	40

# LIST OF TABLES

34 34 34 34 34 34 34 34 34 34 34 34 34 3	
Table 1 Monthly Mean Discharge Data at Tarbert Landing and Simmesport USGS Gauges	.2′ 30
Table 4. Annual Average and Spring Time DIN:DIP Elemental Ratios	
LIST OF FIGURES	
3/4 3/4 3/4 3/4 3/4 3/4 3/4 3/4 3/4 3/4	
Figure 1 Lower Mississippi River and the Lower Atchafalaya River Basin	. 13 . 14 . 16 . 17 . 18 . 18 . 19 . 20 . 20
Figure 14 Average Monthly DIN Mass Transport at Morgan City USGS Monitoring Station 1980-1999 Figure 15 Average Monthly DIP Mass Transport at Morgan City USGS Monitoring Station 1980-1999 Figure 16. Average Monthly DIN and DIP Concentration at Morgan City USGS Monitoring Station 1980 - 19	. 22 . 23 999
Figure 17 DIN and DIP Concentrations at St. Francisville, Belle Chasse and Morgan City 1980 - 1999 Figure 18 Average Monthly DIN/DIP ratios for at St. Francisville, Belle Chasse and Morgan City 1980 to 19	. 24 999
Figure 19 Average Monthly DIN:DIP and DIN:TP Elemental Ratios at Belle Chasse 1980 - 1999 Figure 20 Seasonal Variations in DIN:DIP at St. Francisville	. 26 . 26 . 27
Figure 22 Monitoring Stations where the EPA Data were collected	. 32

## 1 INTRODUCTION

Scientific investigations in the Gulf of Mexico have documented a large area of the Louisiana continental shelf with seasonally-depleted bottom-water oxygen levels (< 2mg/l). Most aquatic species cannot survive at such low oxygen levels. The oxygen depletion, referred to as hypoxia, begins in late spring, reaches a maximum in midsummer, and disappears in the fall. After the Mississippi River flood of 1993, the spatial extent of this zone more than doubled in size, to over 18,000 km², and has remained about that size each year through midsummer 1997. The hypoxic zone forms in the middle of the most important commercial and recreational fisheries in the coterminous United States and could threaten the economy of this region of the Gulf.

Nutrient over-enrichment from anthropogenic sources is one of the major stresses impacting coastal ecosystems. Generally, excess nutrients lead to increased algal production and increased availability of organic carbon within an ecosystem, a process known as eutrophication. There are multiple sources of excessive nutrients in watersheds, both point and non-point, and the transport and delivery of these nutrients are a complex process which is controlled by a range of factors. These include not only the chemistry, but also the ecology, hydrology, and geomorphology of the various portions of a watershed and that of the receiving system. Both the near-coastal hydrodynamics that generate water column stratification and the nutrients that fuel primary productivity contribute to the formation of hypoxic zones. Human activities on land can add excess nutrients to coastal areas or compromise the ability of ecosystems to remove nutrients either from the landscape or from the waterways themselves.

This paper reviews and evaluates existing information regarding the dynamics of nutrients and algal production related to hypoxia in the Gulf of Mexico.

# 2 The Existing Hypoxia Action Plan

#### 2.1 The Assessment Process

As part of a process of considering options for response to hypoxia, the EPA formed the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force during the fall of 1997. The Task Force asked the White House Office of Science and Technology Policy to conduct a scientific assessment of the causes and consequences of Gulf hypoxia through its Committee on Environment and Natural Resources (CENR). A plan to develop the assessment was completed in March of 1998 and presented to a Task Force convened by the EPA which includes federal, state and tribal government representatives. The charge to submit an assessment of hypoxia in the Gulf of Mexico was written into law at the end of the 105th Congress (Section 604a of P.L. 105-383).

In addition to this assessment, P.L. 105-383 called for the development of a plan of action to reduce, mitigate, and control hypoxia in the northern Gulf of Mexico. The Hypoxia Action Plan was to be developed by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. An Integrated Assessment was to be developed to provide scientific information as a basis of the Action Plan.

Under the leadership of the CENR, a Hypoxia Work Group was formed to conduct the hypoxia science assessment. The Work Group was composed of representatives from the Department of Agriculture, the Department of Commerce, the Department of Defense through both the Army Corps of Engineers and the Office of Naval Research, the Department of Health and Human Services through the National Institute of Environmental Health Services, the Department of Interior through the Minerals Management Service and the U.S. Geological Survey, the Environmental Protection Agency, the National Science Foundation, and the Smithsonian Institution.

The goals of the hypoxia science assessment were to document the state of knowledge of the extent, characteristics, causes, and effects (both ecological and economic) of hypoxia in the northern Gulf of Mexico. The assessment compiled some of the existing information on nutrient sources, identified some alternatives for reducing nutrient inputs, and examined the costs and benefits associated with reducing nitrogen loads to surface waters. The assessment of the causes and consequences of Gulf hypoxia was intended to provide scientific information that could be used to evaluate management strategies, and to identify gaps in the understanding of this problem. While the focus of the assessment was on hypoxia in the Gulf of Mexico, the effects of changes in nutrient concentrations and loads and nutrient ratios on water quality conditions within the Mississippi-Atchafalaya riverine systems was also addressed. Much of the history presented in the Introduction was obtained from the NOAA website cited in the Bibliography.

# 2.2 Hypoxia Assessment Reports

As a foundation for the assessment, six interrelated reports that examined various aspects of the hypoxia issue were developed by six teams with experts from within and outside of government. The research teams were to analyze existing data and apply existing models of the watershed-gulf system. They were encouraged to specifically identify additional research or data needed to fill knowledge gaps.

The six completed reports provided the foundation for the final integrated assessment is being used by the Task Force to evaluate alternative solutions and management strategies. The completed reports are as follows:

TOPIC 1. Characterization of hypoxia. This report describes the seasonal, interannual, and long-term variation of hypoxia in the northern Gulf of Mexico, and its relationship to nutrient loadings. It also documents the relative roles of natural and human-induced factors in determining the size and duration of the hypoxic zone. Lead: Nancy Rabalais, Louisiana Universities Marine Consortium.

TOPIC 2. Ecological and economic consequences of hypoxia. This report presents an evaluation of the ecological and economic consequences of nutrient loading, including impacts on Gulf of Mexico fisheries and the regional and national economy. Ecological co-lead: Robert Diaz, Virginia Institute of Marine Science. Economics and co-lead: Andrew Solow, Woods Hole Oceanographic Institution, Center for Marine Policy.

TOPIC 3. Flux and sources of nutrients in the Mississippi-Atchafalaya River Basin. This report identifies the sources of nutrients within the Mississippi/Atchafalaya system and within the Gulf of Mexico with two distinct components. The first identifies where, within the basin, the most significant nutrient additions to the surface water system occur. The second, more difficult component estimates the relative importance of specific human activities in contributing to these loads. Lead: Donald Goolsby, U.S. Geological Survey.

TOPIC 4. Effects of reducing nutrient loads to surface waters within the Mississippi River basin and Gulf of Mexico. This report estimates the effects of nutrient source reductions in the Mississippi-Atchafalaya Basin on water quality in these waters and on primary productivity and hypoxia in the Gulf of Mexico. Modeling analyses was conducted to aid in identifying magnitudes of load reductions needed to effect a significant change in the extent and severity of the hypoxia. Upper watershed co-lead: Patrick Brezonik, University of Minnesota. Gulf of Mexico and co-lead: Victor Bierman, Limno-Tech.

TOPIC 5. Reducing nutrient loads, especially nitrate-nitrogen, to surface water, groundwater, and the Gulf of Mexico. The focus of this report was to identify and evaluate methods to reduce nutrient loads to surface water, ground water, and the Gulf of Mexico. The analysis was not restricted to reduction of sources alone, but included means to reduce loads by allowing the system to better accommodate those sources through, for example, modified hydraulic transport and internal cycling routes. Lead: William Mitsch, Ohio State University.

TOPIC 6. Evaluation of economic costs and benefits of methods for reducing nutrient loads to the Gulf of Mexico. In addition to evaluating the social and economic costs and benefits of the methods identified in topic 5 for reducing nutrient loads, this analysis included an assessment of various incentive programs and any anticipated fiscal benefits generated for those attempting to reduce sources. Lead: Otto Doering, Purdue University.

## 2.2.1 Final Integrated Assessment

A Final Integrated Assessment was published May 2000. This assessment was derived from the six hypoxia assessment reports referenced above. Public comments also were used to contribute to the final integrated assessment.

## 2.2.2 Simple Box Model of the Louisiana Inner Shelf

The development of a simple box model of the eutrophication processes of the Louisiana Inner Shelf was part of the efforts to understand, predict and assess the influence of the Mississippi River nutrient impacts on the Gulf water quality and hypoxia. This model included steady state processes for salinity, phytoplankton, carbon, phosphorus, nitrogen, carbonaceous BOD and dissolved oxygen. The model used a coarse 21 grid representation of the inner shelf from the Mississippi River to the Louisiana Texas border. The sediment oxygen demand and sediment nutrient fluxes are externally specified using observed data and model calibration. The model was calibrated using summer average conditions for 1985, 1988 and 1990. This simple box model was used to determine the hypoxia extent reductions that may occur with various nutrient reduction scenarios.

The Integrated Assessment recommends that:

"For a system as large and complex as the Mississippi-Atchafalaya River drainage basin and the northern Gulf of Mexico, monitoring and research should be integrated using holistic models that simulate our understanding of how the overall system functions and how management practices can best be implemented. Such holistic models include a suite of conceptual, functional, and numerical formulations; integrate research findings; and are tied to monitoring programs designed to both provide input variables and verify model outputs. An effective modeling framework would include models that simulate:

- Transport and transformation of nutrients (nitrogen, phosphorus and silica) from natural, urban, and agricultural landscapes to ground water and surface waters;
- Inputs and outputs of nutrient flow throughout the landscape to improve estimates of nutrient mass balances:
- Biogeochemical cycling and water quality effects of those nutrients on river ecosystems within the drainage basin;
- Oceanographic and climate influences on those nutrients and their impacts on Gulf productivity as they leave the Mississippi and Atchafalaya River system;
- Impact of increased nutrient flux on productivity in the northern Gulf of Mexico ecosystems, including commercially and recreationally important fisheries; and
- Three dimensional coupling of biological and physical processes in the Gulf ecosystem influenced by the Mississippi River discharge."

#### 2.2.3 Hypoxia Action Plan

The Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, at an October 11, 2000 meeting, reached agreement on an Action Plan, based on the Integrated Assessment, to reduce the extent of hypoxia in the Gulf of Mexico.

Under the Plan, current and increased resources would go to voluntary action to reduce excess nutrients in streams and rivers feeding into the Mississippi and Atchafalaya River Basins. These programs would increase the efficiency of farming practices, restore wetlands and riparian buffers, and reduce nutrient discharges from point sources and urban runoff. The Plan also called for funding efforts to facilitate improvement in scientific knowledge and adjustments in management practices.

An adaptive management goal of the Hypoxia Action Plan was to try to reduce nitrogen (Total Nitrogen) in the Mississippi by 30 percent, which researchers believed would significantly reduce the size of the hypoxic zone in the Gulf.

# 2.3 EPA Region 4 Review of the Gulf Hypoxia Issue

Each EPA Region in the Mississippi Basin was instructed to implement the Hypoxia Action Plan. Region 4 enlisted a number of scientists and engineers into a Regional Hypoxia Workgroup charged with assessing the Plan and researching appropriate mechanisms to utilize with Region 4 States to reach the Plan's goals. Several Workgroup members had extensive experience in nutrient reduction strategies but had not previously been involved in the Gulf Hypoxia issue. These scientists and engineers, in preparation for implementation, reviewed the relevant portions of the six Hypoxia Assessment Reports, the Integrated Assessment and the Hypoxia Action Plan.

During 2003, EPA Region 4 initiated a review of a number of issues related to Gulf of Mexico Hypoxia. The initial effort focused on the review of the literature cited in the Hypoxia Assessment Reports. These reports were prepared under the direction of the Committee on Environment and Natural Resources (CENR). The review focused on CENR Reports 1, 3 and 4. The initial review revealed that there were several distinct and conflicting views presented in the Gulf of Mexico hypoxia literature. One view held that most of the primary productivity (algal growth) in the Gulf of Mexico that contributed to hypoxia occurred under mostly "Nitrogen Limited" conditions. Therefore, the obvious and primary answer to the Gulf Hypoxia problem was nitrogen reduction in the Mississippi River Basin. This view placed an emphasis on reducing nitrogen inputs from agricultural operations. This was the position adopted in the 6 CENR Reports, the Integrated Assessment, and the Hypoxia Action Plan.

A conflicting view, supported by numerous studies, was that a significant quantity of primary productivity (algal growth) in the Gulf that contributes to hypoxia occurs under "Phosphorus Limited" or "Phosphorus-Nitrogen Co-Limitation". A corollary view, supported by data, was that the lower Mississippi River had high DIN/DIP ratios during high flows and was therefore not in perfect "Redfield Ratio Balance". These views lead to a conclusion that phosphorus reductions in the Mississippi Basin would perhaps be more effective in reducing Gulf hypoxia than nitrogen reductions.

These two views were in obvious conflict and the need to clarify nutrient limitation was identified in the public comments. Report 1 identifies that hypoxia is due primarily to excess fluxes of nitrogen and phosphorous down the MRB, both of which can be limiting nutrients, but Reports 4-6 address only nitrogen control.

These initial findings and differing conclusions engendered a comprehensive review by Region 4 that included but was not limited to:

- Comprehensive review of the relevant hypoxia literature.
- Analyses of USGS data for the Lower Mississippi River and the Lower Atchafalaya River.
- Analysis of data that had been collected by scientists involved in the Gulf of Mexico hypoxia issue (NOAA Grants).
- Interviews of and assistance from several scientists in the USA currently active in algal productivity research and hypoxia control. Assistance included: providing data and data

analyses, production of graphics, providing literature and literature references, providing abstracts of papers in preparation, critical review of drafts and editing in the development of this paper.

Review of the existing box model used for predicting hypoxia reductions in the Gulf.

# 3 Lower Mississippi and Atchafalaya Rivers: Nutrient Concentrations, Nutrient Mass Transport, and Elemental Ratios

EPA Region 4 used available data collected in the Mississippi and Atchafalaya Rivers and in the Gulf, along with available research papers, to reevaluate previous conclusions regarding the relationship of nutrients to Gulf hypoxia. EPA Region 4 calculated the nutrient loads and the resultant DIN: DIP elemental ratios for key locations in the Mississippi and Atchafalaya Rivers.

#### 3.1 Redfield and Elemental Ratios

For more than 50 years, oceanographers and marine scientists have recognized that the elemental composition of phytoplankton is remarkably similar to that of the seawater in which they are found (Redfield, 1934, 1958, Falkowski, 2000). In his 1958 publication, Albert Redfield established the so-called Redfield elemental ratio (106 C:16 N:1 P, by atoms), based on the concentrations of inorganic nitrogen and phosphate. Although Redfield's analysis dealt exclusively with nitrate to phosphate ratios, it has become common (and accepted) in the literature to include all forms of dissolved inorganic nitrogen (nitrate, nitrite, and ammonium); thus, DIN to DIP ratios are now most commonly used and are used in this paper to evaluate elemental ratios in seawater. Significant deviations from the Redfield ratio provide information on the potential for one nutrient to be used up by phytoplankton while leaving "surpluses" of the other nutrient. Elemental ratio information is often useful for contributing to decisions regarding nutrient management strategies to control the excess growth of phytoplankton.

Gulf hypoxia is attributed to increased phytoplankton production stimulated primarily by excess nutrients delivered by Mississippi River and Atchafalaya River water, especially in spring. Scientific literature shows that by applying the Redfield elemental ratio of DIN:DIP = 16 as a criterion for stoichiometric nutrient balance it can be determined whether N or P is the limiting nutrient which regulates phytoplankton production, with DIN being dissolved  $NH_4-N + dissolved (NO_2+NO_3)-N$  and DIP being dissolved  $PO_4-P$  (e.g., Justic et al., 1995; Turner et al., 2003).

The dissolved inorganic nitrogen (DIN)-dissolved inorganic phosphorus (DIP) elemental ratios (DIN:DIP) were calculated using dissolved N and P measurement parameters:

Ammonia, water, filtered, milligrams per liter as nitrogen (NH<sub>4</sub>-N) Nitrite plus nitrate, water, filtered, milligrams per liter as nitrogen ((NO<sub>2</sub>+NO<sub>3</sub>)-N) Orthophosphate, water, filtered, milligrams per liter as phosphorus (PO<sub>4</sub>-P)

The DIN:DIP elemental ratio was obtained using the formula:

$$DIN:DIP = \frac{\frac{NH_4 - N(mg/L) + (NO_2 + NO_3) - N(mg/L)}{14}}{\frac{PO_4 - P(mg/L)}{31}}$$

The DIN was obtained as the sum of concentrations (in mg/L) of dissolved  $NH_4$ -N and dissolved  $NO_2$ +NO<sub>3</sub>)-N. The DIP is equal to concentration of dissolved  $PO_4$ -P. The equation constants 14 and 31 represent the atomic weights of N and P, respectively. The DIN: DIP elemental ratio was obtained for each simultaneously observed set of parameters listed above. This elemental ratio was calculated as dissolved  $NH_4$ -N plus dissolved  $NO_2$ +NO<sub>3</sub>-N divided by dissolved  $PO_4$ -P multiplied by the constant 31/14.

The following reports the DIN and DIP loads and elemental ratios calculated at the USGS water quality-monitoring sites in the Lower Mississippi River (LMR) and for the Atchafalaya River in Louisiana.

# 3.2 Geographic Setting and Monitoring Station Locations

Figure 1 is a map of the Lower Mississippi River (LMR), the lower Atchafalaya River Basin (ARB), and the coastal areas of Louisiana. The Old River Outlet, a Corps of Engineers (COE) structure, diverts, on average about 25% (Goolsby 13) of the flow of the LMR to the ARB and is located at River Mile 315 near the Mississippi/ Louisiana state line. The ARB includes the drainage of the Red River Basin and other areas and discharges to the coastal waters of the Gulf of Mexico near Morgan City, Louisiana.

# 3.3 Lower Mississippi River Nutrient Analyses

Four Lower Mississippi River water quality and flow monitoring stations were used for the nutrient analyses:

- The Corp of Engineers Tarbert Landing water flow monitoring station located at River Mile 306 just below the Old River Outlet:
- The U.S. Geological Survey (USGS) St. Francisville water quality monitoring station located at River Mile 266:
- The USGS Luling station located at approximately River Mile 121, approximately 35 miles upstream of New Orleans:
- The USGS Belle Chasse water quality station is located at River Mile 76, approximately 10 miles below New Orleans.

The Tarbert Landing water flow monitoring station is maintained by the COE and is located at River Mile 306 just below the Old River Outlet. There are no major streams entering the river below Tarbert Landing and few major diversions, therefore, flows recorded at Tarbert Landing are a reasonable approximation of the flows in the LMR from St. Francisville to Head of Passes. Flow records for all analyses in this report for the LMR were obtained from this station.

The U.S. Geological Survey (USGS) St. Francisville water quality monitoring station is located at River Mile 266 approximately 170 river miles above New Orleans and below both the Old River Outlet and the Tarbert landing water flow monitoring Stations. The St. Francisville USGS station is upstream of approximately 118 major point source dischargers located in the Louisiana Industrial Corridor. The period of record for St. Francisville for most parameters is quite long and the list of parameters is extensive. This is the most downstream USGS station from which data was obtained for the CENR reports.

The Luling USGS station is located at approximately River Mile 121, approximately 35 miles upstream of New Orleans, and has the longest period of record for nitrate in the lower river.

The USGS Belle Chasse water quality station is located at River Mile 76, approximately 10 miles below New Orleans. This station is below all the major cities on the river and below all the major point source discharges. Water flowing past this station transports essentially all the suspended and dissolved constituents from the entire basin, except those transported to the Gulf in the approximately 25% of water diverted to the ARB at the Old River Outlet above Tarbert Landing. There are useful water quality nutrient records at Belle Chasse starting in 1981. Unfortunately, this station was partially terminated in the early 1990s and water quality records

subsequent to that time are sporadic. Due to the paucity of other reliable water quality from below New Orleans in recent years, we have included the recent USGS Belle Chasse data in our analyses. The graphs included in this paper contain fewer data points for the time period after the station was partially abandoned.

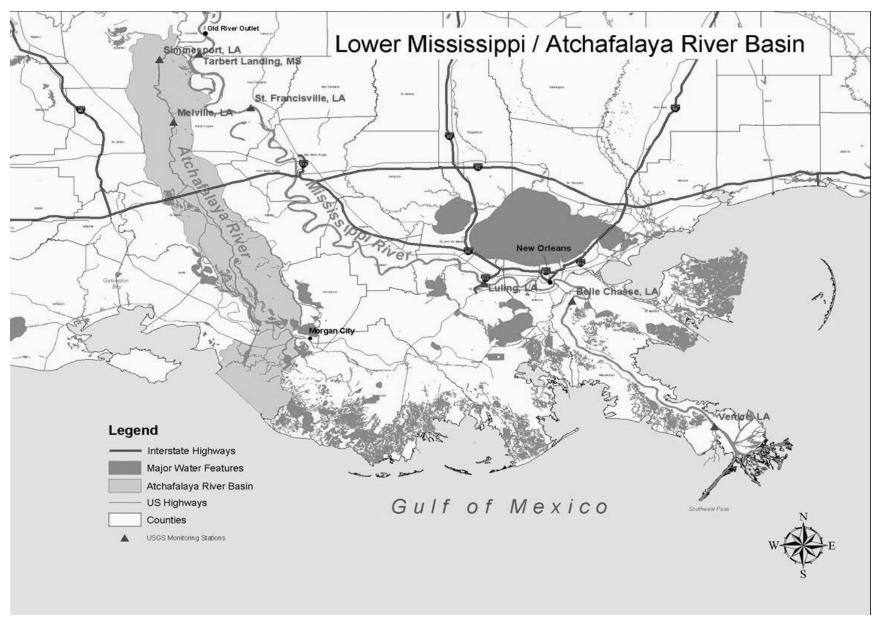


Figure 1 Lower Mississippi River and the Lower Atchafalaya River Basin

Bollinger, et al. (2000) referenced a number of problems with data collected by different entities in the LMR. We also found various problems with data other than the USGS data. Therefore all of our data analyses for the LMR and the ARB were based primarily on USGS data.

River loadings were calculated using FLUX. FLUX is an interactive program designed for use in estimating the loadings of nutrients or other water quality components passing a tributary sampling station over a given period of time. These estimates can be used in formulating reservoir nutrient balances over annual or seasonal averaging periods appropriate for application of empirical eutrophication models. Data requirements include (a) grab-sample nutrient concentrations, typically measured at a weekly to monthly frequency for a period of at least 1 year, (b) corresponding flow measurements (instantaneous or daily mean values), and (c) a complete flow record (mean daily flows) for the period of interest. Using six calculation techniques, FLUX maps the flow/concentration relationship developed from the sample record onto the entire flow record to calculate total mass discharge and associated error statistics. An option to stratify the data into groups based upon flow, date, and/or season is also included. In many cases, stratifying the data increases the accuracy and precision of loading estimates. Uncertainty is characterized by error variances of the loading estimates. A variety of graphic and tabular output formats are available to assist the user in evaluating data adequacy and in selecting the most appropriate calculation method and stratification scheme for each application. FLUX provides information which can be used to improve the efficiencies of future monitoring programs designed to provide data for calculating loadings and reservoir mass balances. (Walker, 1999)

## 3.3.1 Tarbert Landing USGS Gauge (USGS 07373291) Flow Analysis

An analysis of flows at Tarbert Landing shows that the average spring flow of the river is 2.5 to 3 times the average minimal flows. The minimal flows normally occur in August, September, October, and November. Figure 2 depicts the average monthly flows at Tarbert Landing (1973-2002). The flows in the LMR during the spring are normally higher than the remainder of the year. Figure 3 depicts the average annual flows at Tarbert Landing for 1973- 2002.

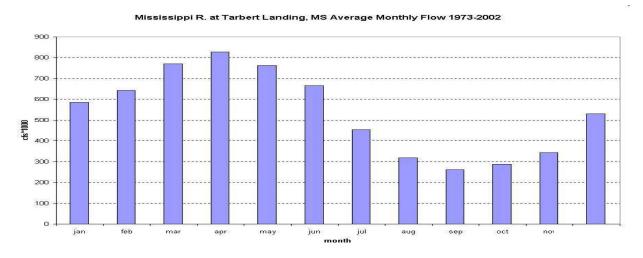


Figure 2 Average Monthly Flows at Tarbert Landing

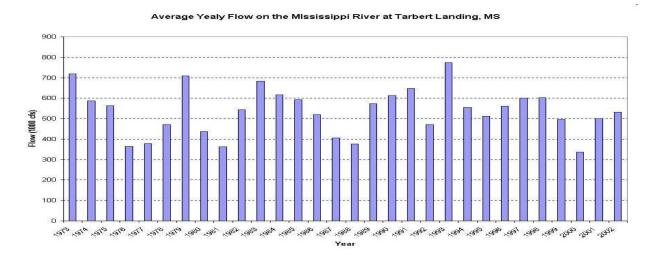


Figure 3 Talbert landing, MS average annual flows for 1973-2002

Table 1 is the observed monthly mean discharges at Tarbert Landing, LA on the Mississippi River (USGS Station 07373291) and Simmesport, LA on the Atchafalaya River (USGS Station 07381490) for various periods. (Winstanley et al, 2003)

Table 1 Monthly Mean Discharge Data at Tarbert Landing and Simmesport USGS Gauges

	1961-2003	961-2003		1981-2001		1992-2001	
Month	Tarbert Landing (10 <sup>3</sup> cfs)	Simmesport (10 <sup>3</sup> cfs)	Tarbert Landing (10 <sup>3</sup> cfs)	Simmesport (10 <sup>3</sup> cfs)	Tarbert Landing (10 <sup>3</sup> cfs)	Simmesport (10 <sup>3</sup> cfs)	
JAN	539.2	238.0	577.5	248.7	529.0	229.4	
FEB	592.3	258.4	648.8	277.7	650.0	277.9	
MAR	736.7	325.3	799.4	343.2	807.7	345.8	
APR	782.1	354.6	777.1	334.2	775.3	333.4	
MAY	730.9	330.6	745.7	320.3	777.0	333.5	
JUN	600.9	273.0	683.5	294.4	669.9	285.6	
JUL	412.9	184.5	479.6	204.8	519.3	221.6	
AUG	299.3	129.2	333.1	141.2	390.5	167.1	
SEP	247.4	104.7	255.3	106.0	261.0	111.9	
OCT	272.9	116.8	281.3	120.0	280.3	120.5	
NOV	323.6	141.1	353.0	153.4	327.5	139.8	
DEC	489.8	215.2	551.2	237.8	510.1	218.4	
MEAN	502.3	222.6	540.5	231.8	541.5	232.1	

#### 3.3.2 The Luling USGS Station Nutrient Analyses

The Luling USGS station, with its longer period of early records, was chosen for portraying some of the nitrate data in the LMR. Nitrate concentrations in the river at Luling, LA increased from 1957 to the mid 1980s, and approximately doubled between the mid-1970s and the mid-1980s (Figure 4). However nitrate concentrations do not appear to have increased significantly in the last 20 years. Therefore for the remainder of the analyses the time period 1980 to 1999 was used since there were no major changes that impacted nitrogen concentrations. It would be difficult to ascribe any changes in hypoxia extent during this period to changes in nitrate. Recent analyses of point source discharges in the LMR (Knecht 2000) showed that nitrate discharges from industries and municipalities below St. Francisville are large but not significant when compared to the quantity of nitrate in the river at St. Francisville.

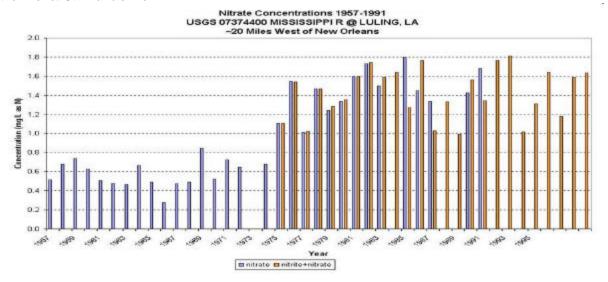


Figure 4 Nitrate Concentrations in the Lower Mississippi River at Luling, LA

## 3.3.3 The U.S. Geological Survey (USGS 07373420) St. Francisville Water Quality Monitoring Station

The USGS chemical data were analyzed for the St. Francisville USGS monitoring station for the period 1980-1999. The FLUX program was used to determine DIN, DIP and TP loads using the continuous flows from the Talbert gauge. Figure 5 depicts the seasonal variation and Figure 6 the average monthly mass transport of Mass DIN at St. Francisville for the period 1980-2001. DIN mass transport is higher in the spring when the river flows are higher and much reduced in the late summer when flows are lower. Therefore, the mass transport of nitrate in the LMR appears to be strongly flow related. Lohrenz et al. (1999) and others have also correlated nitrate transport with flow in the LMR. Fisher, et al. (1992) provide excellent analyses of the concentration and mass transport of constituents to Chesapeake Bay and demonstrates that constituents, where the flow and mass transport are positively correlated, often correspond to sources dominated by non-point origins.

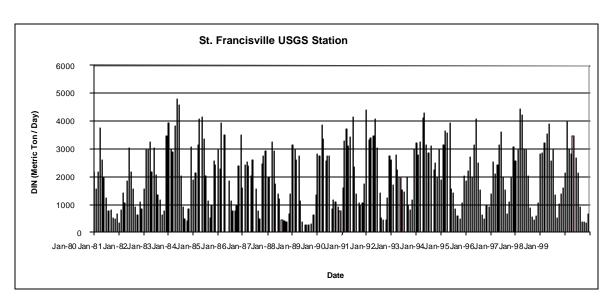


Figure 5 Average Monthly DIN Mass Transport at St. Francisville USGS Monitoring Station 1980 - 1999

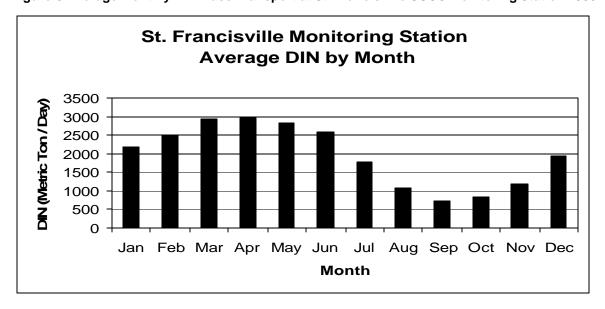


Figure 6 Average Monthly DIN Mass Transport at St. Francisville USGS Monitoring Station 1980 - 1999

The LMR is transporting a tremendous load of nitrogen to the Gulf. (Figure 6) The LMR transported an annual average of 728,000 metric tons of dissolved inorganic nitrogen (DIN) each year during that period. That data also shows that average DIN transport varied from 3100 metric tons per day during April to a low of 700 metric tons per day during September. This strong seasonal variation in DIN transport has important water quality consequences for the Gulf.

An analysis of the USGS phosphorus data for 1980 to 1999 at St. Francisville shows that the river, at that location, transported of an annual average of 35,400 metric tons of dissolved inorganic phosphorus (DIP). The average DIP transport varied from a maximum of 130 metric tons per day during April to a low of 42 metric tons per day during September. Figure 8 depicts the average monthly DIP mass transport at St. Francisville during the period of record 1980 to 1999. The mass transport of phosphate shows less month to month variation than DIN. This flatter mass transport profile for phosphate would be consistent with origins for phosphate that are

influenced by point sources. Fisher et al. 1992, studying rivers tributary to the Chesapeake Bay, found a similar transport profile for pollutants with a largely point source origin. Also an analysis of DIN and DIP monthly concentrations transport at St. Francisville during the period 1980 to 1999 (Figure 7) shows that phosphorus increases and nitrogen decreases during the low flow months of August – November. The distinct phosphorus concentration profile indicates that phosphorus may have largely point source origins, while nitrogen concentration is strongly related to flow. This issue requires additional analysis.

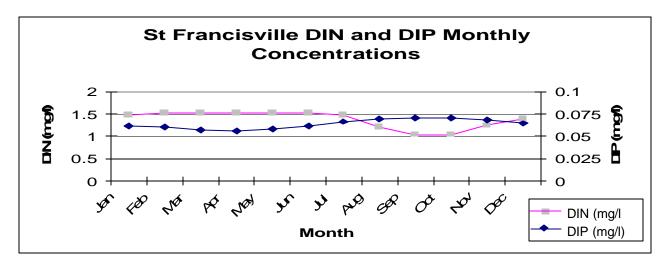


Figure 7 Average Monthly Concentrations at St Francisville USGS Monitoring Station 1980 - 1999

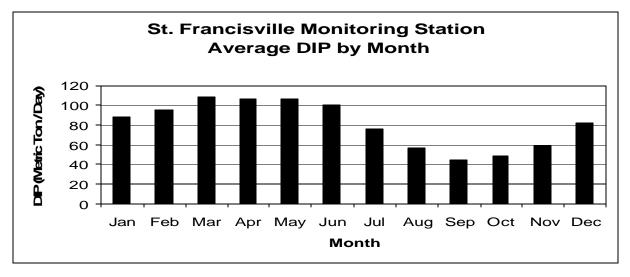


Figure 8 Average Monthly DIP Mass Transport at St. Francisville USGS Monitoring Station 1980-1999

Figure 9 shows Total Phosphorus (TP) transport by month. Figure 9 depicts a seasonal pattern for TP mass transport. We could not locate any published studies that evaluated the bio-availability of TP for the LMR or the ARB. The TP average annual load is 100,400 metric tons about 3 times the amount of DIP.

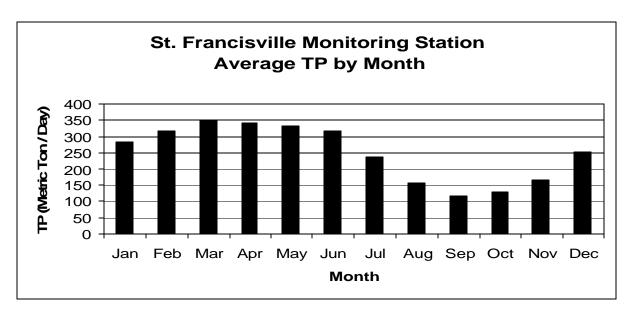


Figure 9 Average Monthly TP Mass Transport at St. Francisville USGS Monitoring Station 1980-1999

## 3.3.4 The USGS Belle Chasse Water Quality Station Nutrient Analyses

The USGS Belle Chasse water quality station is located at River Mile 76, approximately 10 miles below New Orleans. This station is below all the major cities on the river and below all the major point source discharges. Water flowing past this station transports essentially all the suspended and dissolved constituents from the entire basin, except those transported to the Gulf in the approximately 30% of water diverted to the ARB at the Old River Outlet above Tarbert Landing. Figure 10, Figure 11 and Figure 12 depict the monthly DIN, DIP and TP mass transport for the period 1981-1999 at Belle Chasse. The annual average FLUX calculated mass transport loads for DIN, DIP and TP are 2,017; 114 and 390 metric tons per day respectively.

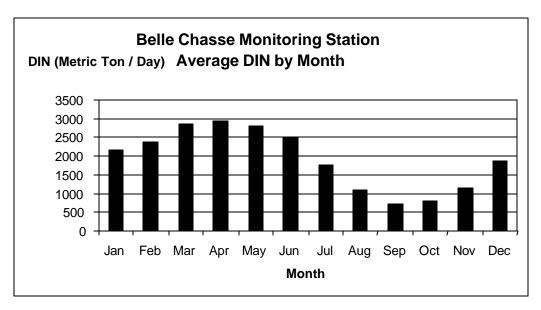


Figure 10 Average Monthly DIN Mass Transport at Belle Chasse USGS Monitoring Station 1980-1999

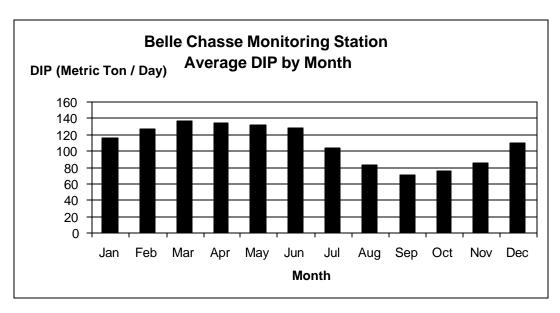


Figure 11 Average Monthly DIP Mass Transport at Belle Chasse USGS Monitoring Station 1980-1999

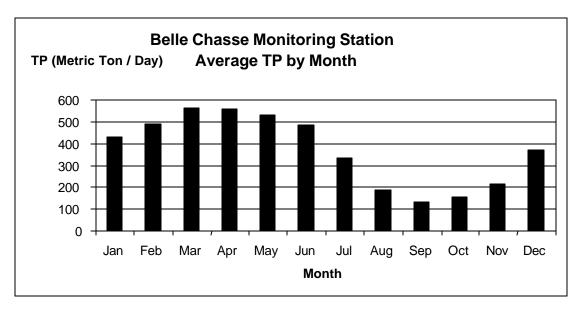


Figure 12 Average Monthly TP Mass Transport at Belle Chasse USGS Monitoring Station 1980-1999

The average measured DIN concentration at Belle Chasse during the period 1980 to 1999 was approximately 1.6 mg/L, (Table 2) which is equivalent to 114  $\mu$ M DIN. Dortch, et al. (1994), indicated that 1.0  $\mu$ M DIN was the lowest DIN concentration that phytoplankton were capable of extracting from seawater. Therefore, the LMR is providing DIN to the Gulf at a concentration approximately 114 times the minimal concentration necessary to sustain the growth of phytoplankton in a coastal environment. This assumes that light and other nutrients are not limiting the phytoplankton growth.

Table 2 Mean Chemical Concentrations at Belle Chasse USGS Monitoring Station 1980 - 1999

Parameter Name	Units	# Observations	Mean
NH3	mg/L	136	0.07
NO2NO3	mg/L	513	1.46
P ORTHO	mg/L	111	0.09
P_TOTAL	mg/L	362	0.27

Figure 13 indicates that phosphate concentration appears to be inversely correlated with flow, while nitrogen concentrations are related to flow. Phosphate concentrations show relatively small month to month variation, again indicative of a parameter that may be influenced by point sources. However, as previously stated, this issue requires additional analysis.

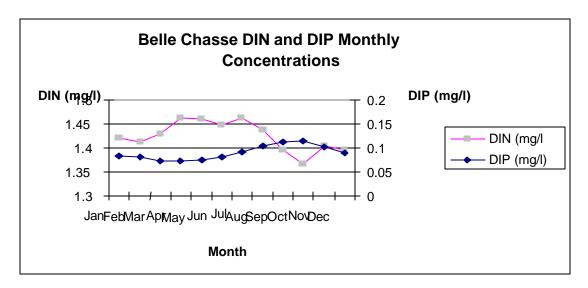


Figure 13 Average Monthly DIN and DIP Concentration at Belle Chasse USGS Monitoring Station 1980 - 1999

The average DIP concentration at Belle Chasse during the period 1980 to 1999 was approximately 0.09 mg/L. (Table 2). EPA Region 4 scientists consider this concentration to be "elevated". This concentration of DIP is capable of contributing to excess phytoplankton production (personal communication, Robert Quinn EPA Region 4, 2003). This is equal to 90 micrograms/L or approximately 2.9  $\mu$ M. Dortch, et al. (1994), believed that 0.2  $\mu$ M phosphate was the lowest concentration that phytoplankton were capable of extracting phosphate from seawater. Therefore, the LMR is providing phosphate at a concentration approximately 15 times the concentration necessary to sustain the minimal growth of phytoplankton in a coastal environment.

EPA R4 analysis of USGS data for St. Francisville and Belle Chasse for the period 1981-1999 indicates that approximately 34% of the phosphate in the river at Belle Chasse entered the river below St. Francisville during that time period. Additional analyses of the USGS data and other data should be accomplished to evaluate possible recent trends in phosphate concentrations and mass transport in the LMR. Re-establishment of a full

time USGS water quality station at Belle Chasse below New Orleans would be very helpful. However, monitoring of large sporadic discharges, typical of discharges from fertilizer plants, requires special consideration.

Table 3 Annual loads (Metric Tons/Day) at St. Francisville and Belle Chasse USGS Monitoring Stations 1980 - 1999

Parameter	St. Francisville	Belle Chasse
DIN	2049	2017
DIP	85	114
TP	262	390

## 3.3.5 Atchafalaya River Nutrient Analyses

Similar nutrient analyses were conducted in the Atchafalaya. The USGS station at Morgan City, LA provided water quality data for the lower Atchafalaya River at a point near where the river discharges into the coastal waters of the Gulf, approximately 80 miles southwest of New Orleans River and the COE station at Simmesport, LA provided flow records for the Atchafalaya River.

Figure 14 and Figure 15 show the monthly transport of DIN and DIP for the Atchafalaya River at Morgan City. The annual average FLUX calculated mass transport loads for DIN equal to 612 metric ton per day and DIP equal to 28 metric ton per day.

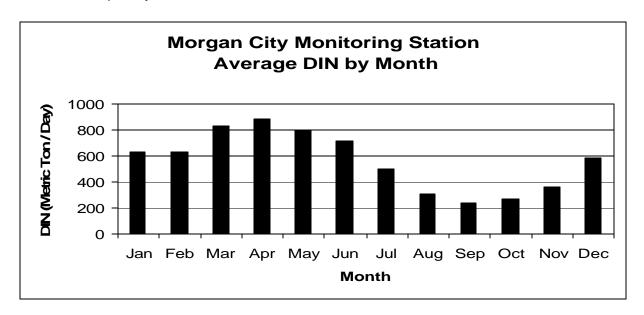


Figure 14 Average Monthly DIN Mass Transport at Morgan City USGS Monitoring Station 1980-1999

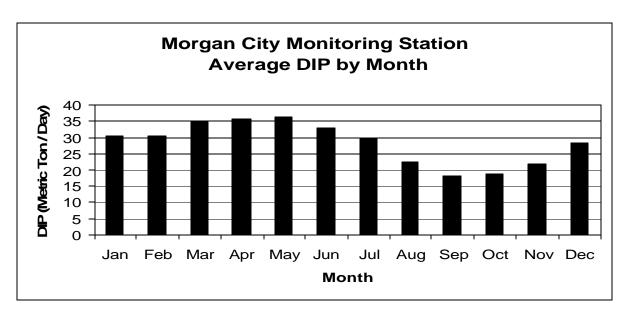


Figure 15 Average Monthly DIP Mass Transport at Morgan City USGS Monitoring Station 1980-1999

Figure 16 shows the monthly concentration of DIN and DIP for the Atchafalaya River at Morgan City. The average DIN concentration at Morgan City, LA during the period 1992 to 1999 was approximately 1.0 mg/L or 71  $\mu$ M. Therefore, the ARB is transporting DIN at approximately 71 times the concentration necessary to sustain the minimal growth of phytoplankton in a coastal environment. The annual average phosphate concentration at Morgan City during the period 1980 to 1999 was approximately 0.06 mg/L. This concentration of DIP is capable of contributing to excess phytoplankton production (personal communication, Robert Quinn EPA Region 4, 2003). This is equivalent to approximately 1.8  $\mu$ M. Therefore, the ARB is transporting phosphate to the Gulf at approximately 8 times the concentration necessary to sustain the minimal growth of phytoplankton in a coastal environment.

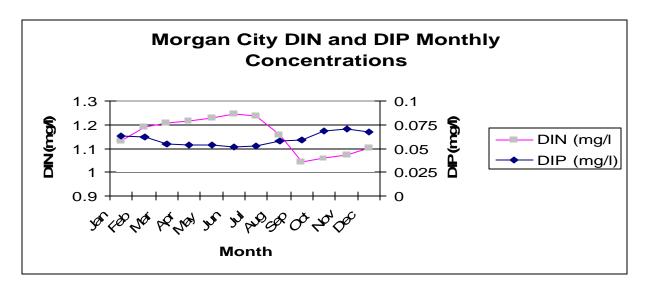


Figure 16. Average Monthly DIN and DIP Concentration at Morgan City USGS Monitoring Station 1980 - 1999

# 3.4 DIN and DIP Limiting Concentration and Elemental Ratios in the LMR and ARB

Monitoring stations Belle Chasse and St. Francisville in the LMR and Morgan City in ARB were used to characterize the DIN and DIP elemental ratios. DIN and DIP average concentrations were calculated using the FLUX program for the period of 1980 to 1999.

Figure 17 depicts the average DIN Concentration and DIP Concentration at St. Francisville, Belle Chasse and Morgan City. This figure suggests that DIN and DIP are being transported to the Gulf far in excess of that required to sustain the growth of phytoplankton. This analysis shows that large quantities of DIN relative to DIP are being transported to the Gulf. This analysis also suggests that DIN reductions of a magnitude necessary to have any significant impact on phytoplankton growth in the Gulf of Mexico would be a daunting task. Phosphorus reductions necessary to impact phytoplankton growth in the Gulf would apparently be very difficult but perhaps more realistic. These issues require additional analysis.

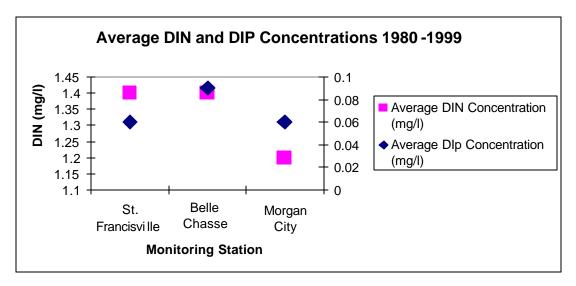


Figure 17 DIN and DIP Concentrations at St. Francisville, Belle Chasse and Morgan City 1980 - 1999

Figure 18 depicts the DIN/DIP ratios at St. Francisville, Belle Chasse and Morgan City for 1980 to 1999. The elemental ratios are especially high (average about 45 to 60 for Feb-May) during the spring when the river flows are high. The high ratios show that large quantities of bio-available nitrogen compared to bio-available phosphorus are transported to the Gulf during the high spring river flows. The elemental ratios during the spring deviate from the Redfield proportions (16:1) by a factor of approximately 3. Lohrenz et al. (1999), also reported very high elemental ratios in the LMR and found that the high ratios were strongly correlated with high flows.

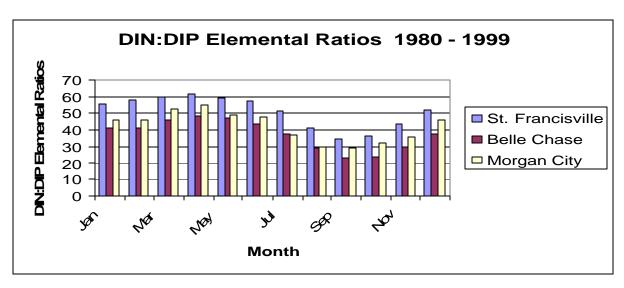


Figure 18 Average Monthly DIN/DIP ratios for at St. Francisville, Belle Chasse and Morgan City 1980 to 1999

Justic et al. (1995), Rabalais et al. (1999), Rabalais and Turner (2001), and Rabalais et al. (2002) reported that the elemental ratios for the LMR vary around the Redfield ratio (approximately 16:1) on a seasonal basis. Elemental ratios reported by Rabalais and co-workers and utilized in the CENR for the LMR were based on DIN/TP. However, elemental ratios reported for the Gulf were based on DIN/DIP. A review of approximately 50 other scientific publications related to phytoplankton production/hypoxia provided no other instance where dissolved inorganic nitrogen and total phosphorus was used for the computation of Redfield ratios. CENR itself recognizes that "Orthophosphate is the principal form of dissolved P and the only form of P that can be utilized by algae, bacteria, and plants (Correll 1998)." (Goolsby et al. 1999, page 25. Section 3.3).

Raschke and Schultz (1987), in their review of the EPA algal growth potential test, (Miller et al. 1978) provide information on the often limited quantity of bio-available phosphorus in total phosphorus. That paper provides scientific rationale for utilizing dissolved inorganic phosphorus rather than total phosphorus in the computation of Redfield ratios. Further, Turner, et al. (2003) and others state that Redfield ratios should be calculated by using the formula DIN/DIP.

Calculations using DIN/TP show that this ratio varies seasonally around the 16:1 ratio. However, DIN/DIP ratios are substantially higher than 16:1, varying seasonally around 45:1. Use of DIN/DIP indicates that nutrient concentrations in the LMR at St. Francisville were not in Redfield balance during this time period. During late winter and early spring, the LMR was "out of ideal ratio" by a factor of more than 4; in other words, there was an excess of DIN relative to DIP. The conclusion (CENR Report, Section 5.3.4, pages 51-54) that the waters in the Lower Mississippi River are "in nutrient balance", based on DIN/TP analysis, should be re-evaluated.

Figure compares DIN:DIP to DIN:TP elemental ratios for Belle Chasse.

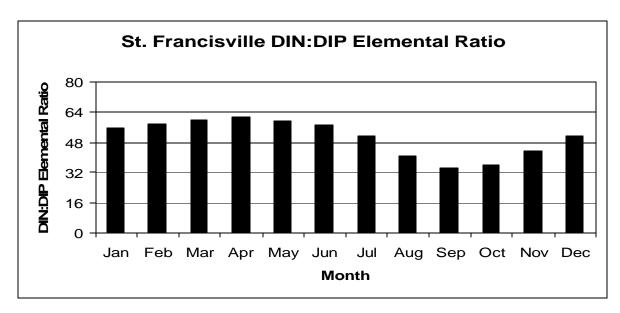


Figure 19 Seasonal Variations in DIN:DIP at St. Francisville

Figure 19 depicts the seasonal variation in elemental ratios (DIN: DIP) at St. Francisville for the period 1980-1999. The DIN/DIP ratios exceeded Redfield proportions throughout all seasons at St. Francisville, and are higher than at Belle Chasse (Figure and Figure 19). DIN is overabundant, relative to DIP, in the water discharged from the Mississippi River. The difference in DIN/DIP ratio between St. Francisville and Belle Chasse, may indicate that large quantities of phosphate were being added to the river below St. Francisville.

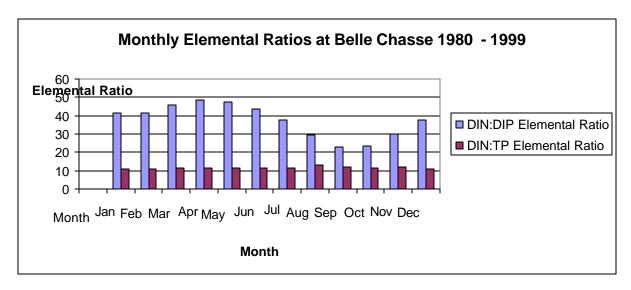


Figure 20 Average Monthly DIN:DIP and DIN:TP Elemental Ratios at Belle Chasse 1980 - 1999

Table 4 depicts DIN/DIP elemental ratios for at St. Francisville, Belle Chasse and Morgan City for 1980 to 1999. The elemental ratios are especially high (average about 47 to 60 for Feb-May) during the spring when the river flows are high and the majority of the nutrients are delivered to the Gulf to feed the spring phytoplankton production.

The annual average elemental ratios at these stations exceed Redfield proportions by a factor of approximately 2.75. Therefore, in order to bring the LMR into the Redfield nutrient balance (16:1 DIN/DIP ratio), average annual DIN concentrations in the LMR would have to be reduced approximately 64%. DIN concentrations would have to be reduced as much as 70% during the critical spring months. In order to bring the N/P ratios into the range of nitrogen/phosphorus "ratio" limitation (N/P ratio 10:1), which is thought to be "potentially nitrogen limiting" (Dortch and Whitledge, 1992), average annual DIN concentrations would have to be reduced approximately 78% and DIN concentration during the critical spring period would have to be reduced as much as 88%. These reductions are comparable to those calculated by Winstanley. (Winstanley et al. 2003). DIN reductions of this magnitude may be either technically infeasible or cost prohibitive.

Table 4. Annual Average and Spring Time DIN:DIP Elemental Ratios

	St. Francisville	Belle Chasse	Morgan City	Three Station Average
Average lemental	51	37	42	44
 Average lemental	60	47	52	53

Figure 19 depicts the Belle Chasse mean monthly DIN: DIP elemental ratio with and without a 20% reduction in DIN, which is approximately equivalent to the 30% reduction in total nitrogen recommended in the EPA Hypoxia Action Plan. A 20% reduction in DIN would have relatively little impact on the DIN/DIP ratio of LMR water discharged to the Gulf of Mexico.

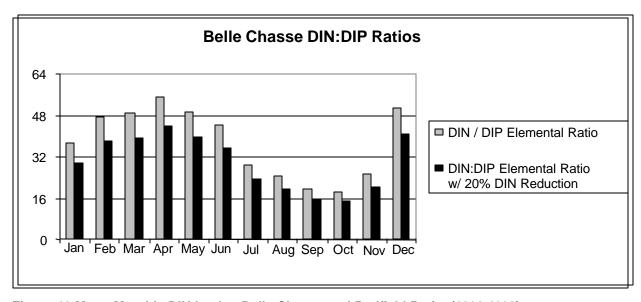


Figure 19 Mean Monthly DIN load at Belle Chasse and Redfield Ratios(1992-1999).

# 3.5 Bio-available Nitrogen and Phosphorus

Information on bio-available phosphorus and nitrogen in water in the LMR and ARB will apparently not be available until the scientific community conducts the appropriate bio-availability studies. Fisher, et al. (1999), conducted extensive bio-availability studies for the Chesapeake Bay and these studies have produced knowledge essential for improved nutrient control strategies in Chesapeake Bay. The advantages of such studies were discussed by Raschke and Schultz, (1987).

There is an abundance of literature that considers the bioavailability of phosphorus from agricultural operations, including Sharpley et al. (1992) and Sharpley and Smith (1992). There is also abundant literature that considers the bioavailability of phosphorus from municipal wastewater, including Ekholm and Krogerous (1998). Elemental ratio analyses to assist in the development of phosphorus and/or nitrogen reduction plans should be based on the bio-available nitrogen/bio-available phosphorus ratio (BAN/BAP)

Most of the past studies focus on measurements derived a short distance from the source. These study results have very little meaning in a system as vast as the Mississippi and Atchafalaya Basins. Bio-availability of nitrogen and phosphorus in the LMR, the ARB, and the Gulf is complicated by the very large geographic scale and will require carefully designed research. The most important area for determining bioavailability is in the area of phytoplankton utilization.

# 4 GULF OF MEXICO PRIMARY PRODUCTIVITY AND HYPOXIA

The Lower Mississippi/Atchafalaya River system (MARS) discharges an average of 952,700 metric tons of nitrogen as nitrate each year (CENR Report 3) Goolsby, et al., 1999). Nitrate concentrations and mass flow are generally highest during the spring and early summer. Dortch and Whitledge (1992) considered that concentrations equal to or less than 1.0 micro-molar dissolved inorganic nitrogen were potentially limiting for phytoplankton growth. The MARS discharges an average of 41,770 metric tons annually of phosphorus as orthophosphate (Goolsby et al. 1999) Dortch and Whitledge (1992) designated 0.2 micro-molar phosphorus as a threshold for potential limitation of phytoplankton growth by phosphorus. EPA shipboard surveys (R. Greene, unpublished data) of nutrient concentrations at the mouth of the Mississippi River revealed near-surface DIN and DIP concentrations during June 2003 frequently far in excess of these threshold values. Figure 22 depicts the monitoring stations where the EPA data was collected.

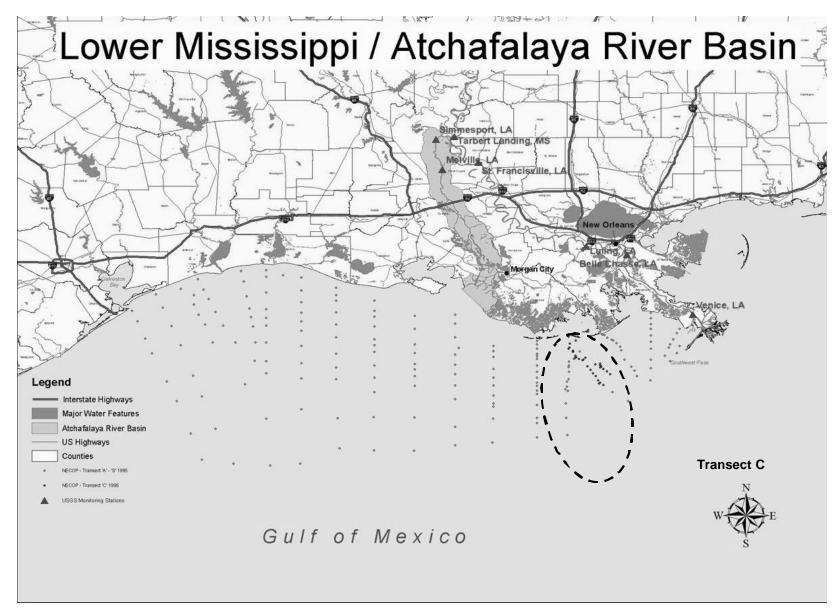


Figure 20 Monitoring Stations where the EPA Data were collected

It is readily apparent that these rivers, during the spring and early summer, provide large nitrogen and phosphorus loads to the Gulf of Mexico. Uptake and elemental composition of nitrogen and phosphorus in phytoplankton in the open ocean are usually near the Redfield ratio of 16:1 dissolved inorganic nitrogen (DIN): dissolved inorganic phosphorus (DIP) (Redfield, 1958). Correll (1998) discusses conditions where DIN/DIP ratios can deviate significantly from the Redfield ratio.

During the spring and early summer in waters influenced by the Mississippi River, ratios of ambient concentrations of DIN:DIP have often been found to be much higher than the Redfield ratio (Lohrenz et al. 1999, Ammerman, et al. 1992, Chen, 2000, Smith and Hitchcock, 1994, Dortch et al. 1992, Nelson 2003, (personal communication), and Dortch 2003 (personal communication).

Scientists have been studying the growth of phytoplankton in the Gulf of Mexico for many years. Riley (1937) provided one of the first reports on phytoplankton concentrations off the Louisiana coast. He found that the quantity of phytoplankton appeared to be correlated with the concentration of orthophosphate. In the early 90s, considerable effort was focused on determining what environmental factors in the Gulf regulated phytoplankton growth and primary production. Much of this research has evaluated the theory that nitrate-nitrogen was the primary limiting nutrient in the Northern Gulf of Mexico. This theory formed the basis for arguments that the large loading of nitrate-nitrogen to the Gulf of Mexico from the Mississippi and Atchafalaya Rivers was contributing to excessively high phytoplankton production in the northern Gulf of Mexico. This high phytoplankton production has been implicated in the chronic seasonal hypoxia that has been observed off Louisiana. This line of reasoning has lead to a management strategy involving the reduction of the nitrogen transported to the Gulf, especially during the spring, in order to reduce phytoplankton production and therefore mitigate the hypoxia problem. Based on largely empirical models, a target reduction of 30% total nitrogen has been suggested in order to reduce the extent of hypoxia to "1970's" levels. (CENR Reports 1 and 4, the Integrated Assessment, and the Hypoxia Action Plan). This 30% reduction was also subsequently discussed in numerous publications by Rabalais and associates.

A series of investigations during the 1990's conducted studies to identify which nutrients were limiting phytoplankton growth. Dortch and Whitledge (1992) attempted to identify which nutrients were limiting. Observations made during cruises conducted in summer 1987 and spring 1988 off of Southwest Pass revealed sharp gradients with salinity, turbidity, and nutrients as river water from Southwest Pass mixed with Gulf of Mexico water. As the turbidity decreased, the corresponding increased penetration of sunlight into the nutrient-enriched water stimulated high levels of phytoplankton growth and production. At stations further offshore, nutrient concentrations were reduced to very low levels due to the combination of phytoplankton growth and dilution with high salinity Gulf of Mexico water having very low nutrient concentrations. Using two different approaches to assess nutrient limitation, Dortch and Whitledge (1992) found that the ratio of intracellular free amino acids to protein, an index of nitrogen limitation, did not support the view that nitrogen limitation was widespread. They also used an indirect method to infer which nutrients were limiting, based on concentrations and ratios of inorganic nutrients. This latter approach indicated that potential limitation by phosphorus was more likely than nitrogen limitation in areas of low salinity, especially during spring. The potential for nitrogen limitation was more prevalent in higher salinity waters further offshore, especially during the late summer. Only 6% of all samples taken during the three cruises provided indications of potential nitrogen limitation.

The potential importance of phosphorus as a limiting nutrient has been reported by other studies and this was reviewed in CENR Report 1. Lohrenz et al. (1999) used an indirect approach similar to that of Dortch and Whitledge (1992) to infer which nutrients were limiting in the northern Gulf of Mexico. They also found evidence for potential phosphorus limitation in lower salinity waters, particularly in spring. Lohrenz et al. (1999) recommended phosphorus reduction in the Mississippi River as a potentially effective measure to control the excess phytoplankton production, especially during the spring and early summer. Smith and Hitchcock (1994) conducted nutrient enrichment bioassays in the Gulf of Mexico during March and September 1991 and May 1992. Their findings were consistent with phosphorus limitation during the spring, especially in the lower salinity

waters, and nitrogen limitation in the fall. Other evidence for phosphorus limitation in Mississippi River plume waters comes from reported high rates of phosphorus turnover during July and August 1990 and September 1991, particularly in low salinity waters (Ammerman, 1992). Ammerman (1992) also found high activities of alkaline phosphatase, an enzyme that is induced in some phytoplankton under low phosphorus conditions.

A substantial body of unpublished work provides additional evidence that phosphorus may limit primary production in northern Gulf of Mexico shelf waters. Dr. Dave Nelson and Dr. Quay Dortch (personal communications, 2003) recently completed a three year extensive investigation in the northern Gulf. They collected nutrient data and also conducted nutrient addition studies. According to Dr. Nelson, "There are extensive areas of the Northern Gulf, with very high phytoplankton productivity and where there is a great excess of DIN relative to DIP. In these areas of high DIN/DIP ratios, phytoplankton growth was enhanced more by additions of phosphorus than by additions of nitrogen". Evidence for phosphorus limitation was more prevalent in the lower salinity waters and during the spring and early summer." Dr. Nelson also found that evidence of nitrogen limitation was more prevalent during the late summer and fall. Dr. Quay Dortch (personal communication, 2003) confirmed these observations.

Another investigator, Dr. James Ammerman (personal communication, 2003) has recently completed extensive surveys in the northern Gulf. He conducted surveys characterizing alkaline phosphatase activities, in many cases at the same locations and days as the studies by Nelson and Dortch. Ammerman found extensive areas of high alkaline phosphatase activities consistent with phosphorus limitation. Ammerman found that the areas with high alkaline phosphatase activity correlated well with areas of high DIN:DIP ratios, based on analyses of his own nutrient data and nutrient analyses by Nelson and Dortch. Subsequent to the CENR reports, Chen (2000) found evidence for extensive phosphorus limitation in the northern Gulf.

Data were acquired from a NOAA website (http://www.aoml.noaa.gov/ocd/necop/) for three years, 1994, 1995, and 1997, which was part of an extensive data set on nutrient concentrations in the Gulf of Mexico spanning many years (Hendee,1994, and Hendee, personal communication, 2003) Dr. Nancy Rabalais, (Louisiana University Marine Consortium), Dr. R. Eugene Turner, (Louisiana State University), and Dr. William W. Wiseman (Louisiana State University) compiled this data through funding provided by NOAA.

These data were subsequently analyzed by EPA scientists. In addition, some of the data was analyzed by Dr. Steven Lohrenz, University of Southern Mississippi, and Dr. Rodney Powell, Louisiana University Marine Consortium. The data were from Transect C (Figure 22), which starts in the inshore waters (water depth 5.4 meters) off Terrebonne Bay, near Chauvin, Louisiana and runs southward for approximately 50 miles to an offshore location where the water depth is approximately 45 meters.

The DIN and DIP surface data from 1994 to 1997 were used to determine DIN/DIP elemental ratios for each month that data were collected. The results, depicted in Figure 21, show high DIN: DIP ratios during the spring and early summer and lower ratios during the late summer and fall. The DIN: DIP ratios during the spring and late summer were often well above the Redfield ratio of 16:1, indicative of the potential for phosphorus limitation. The lower DIN: DIP ratios during the late summer and fall were closer to the Redfield ratio, and this would be consistent with either phosphorus or nitrogen limitation, or co-limitation by both. More data and data analyses are needed to determine if during the late summer the Gulf is phosphorus limited, or co-limited. The more recent data gives no clear indication that the Gulf is a nitrogen limited system.

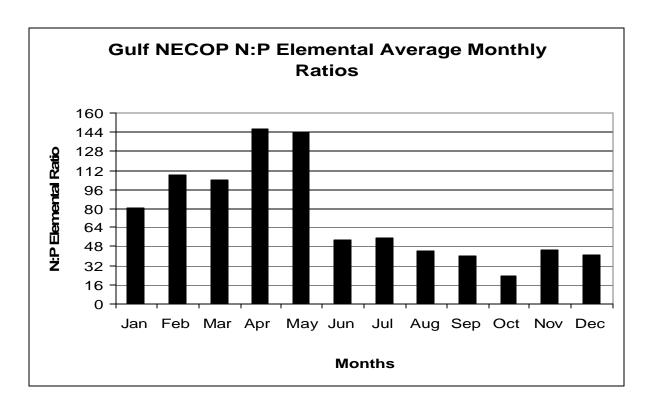


Figure 21 DIN/DIP Elemental Ratios from Transect C Sampling, 1994, 1995 and 1997

Highest chlorophyll concentrations along Transect C were observed during the spring and early summer of 1997(Figure 22), and this would be expected to coincide with the period of highest productivity. Consistent with this view, in an analysis of monthly composite chlorophyll data for Transect C stations C6, C6A, and C6B for the years 1985-1997, Rabalais and Turner (2001) reported that chlorophyll concentrations were generally highest during April and May and lower in the late summer months. This would suggest that, at these stations along Transect C, a large portion of the annual primary productivity occurs during the spring and early summer. Rabalais and Turner (2001) also refer to several studies showing relatively high abundance of copepod zooplankton, and the production of copepod fecal pellets during the spring and early summer.

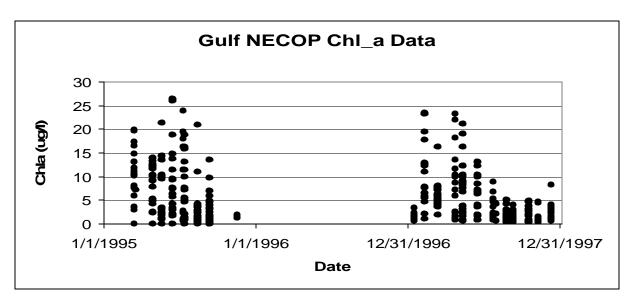


Figure 22 Chl\_a Concentrations along Transect C, 1995 and 1997

CENR Report 1 (Section 6.5, pages 75-77) concluded that the phytoplankton, copepod zooplankton, and copepod fecal pellets were produced in quantity during the spring and early summer growing season. This report also concluded that this productivity was the likely source of organic matter that sinks to the lower water strata and decays. The report also concluded that this organic matter produced during the spring and early summer consumes dissolved oxygen and is a major factor contributing to hypoxia.

All the numerous published studies, unpublished studies, and our own analysis of unpublished LUMCON/Louisiana State University data indicate a potential for phosphorus limitation in the lower salinity waters of the northern Gulf of Mexico during the spring and early summer. This low salinity area also appears to be the geographic area where a substantial portion of the primary productivity occurs that contributes to hypoxia.

Nitrogen limitation appears to be confined to the higher salinity areas, especially during the late summer and fall. The higher salinity areas usually have low nutrient concentrations due to nutrient depletion by phytoplankton and dilution with low nutrient offshore waters. These high salinity areas normally exhibit low primary productivity. Likewise, primary productivity during the late summer and fall is generally lower than in the spring and early summer. Due to the relatively low productivity in high salinity areas and seasons when nitrogen limitation may be prevalent, the contribution of primary productivity under nitrogen limiting conditions to hypoxia is highly questionable. To our knowledge, it has not been demonstrated that primary productivity under nitrogen limiting conditions is the major source of organic matter leading to oxygen depletion and hypoxia in the northern Gulf of Mexico.

The pattern of phosphorus limitation during the spring and early summer and nitrogen limitation during the late summer and fall is not unique to the Mississippi and Atchafalaya river system. Fisher et al. (1992) described such a pattern for the Chesapeake Bay, based on comprehensive water quality sampling and nutrient loading studies. Fisher et al. (1999) also conducted comprehensive and very sophisticated nutrient addition studies for the Chesapeake Bay. These studies confirmed extensive phosphorus limitation in the Chesapeake Bay during the spring and early summer and nitrogen limitation during the late summer and fall. These nutrient addition studies were better designed and much more comprehensive than any conducted to date for the Gulf hypoxia issue. Accordingly, decreasing phosphorus loading to the Chesapeake Bay, to control excess phytoplankton production during the spring and early summer, is an integral part of the control strategy.

# 5 Additional Data Collection and Analysis, Additional Water Quality Modeling and Additional Research Needs

The Region believes that significant data and knowledge gaps exist such that additional appropriate data collection and analysis, additional water quality modeling and additional research are justified. The needs are:

- 1) Gather all available data, both loadings to the Gulf and the Gulf data in one database and conducting appropriate data analyses and statistics on these data;
- 2) collect more data and information on the Gulf in a comprehensive and coordinated effort among all stakeholders and agencies;
- 3) develop a credible hydrodynamic and water quality model to help understand the complexities of the system and as a tool to help making future management decisions;
- 4) develop a sources, fate and transport macro model for the Mississippi River Basin, and
- 5) continue to conduct and support research to better our understanding of the Gulf nutrient and algal dynamics.

One of the basic critical needs is the determination of the ratio of bio-available nutrients in the Lower Mississippi and Atchafalaya Rivers. The bio-availability of nutrients was not considered in the CENR reports. The EPA Algal Growth Potential Protocol that was published in 1978 could be used to assist in these studies.

# 5.1 Data Collection and Data Analyses

#### 5.1.1 Better Characterization of the Gulf Hypoxia Zone

In the more marine segment of the plume, N reductions could possibly have a significant impact in reducing primary production. However, the relative importance to Gulf hypoxia, of primary productivity in the higher salinity areas, especially during the summer and fall, relative to the much higher primary productivity that occurs in the lower salinity areas, especially during the late winter and spring have not been adequately considered. Stable C and N isotope studies examining the formation of new production could help address this knowledge gap. Current modeling efforts aiming to answer this important question are only as good as the data needed to establish and verify them.

The present once per year shelf-wide monitoring efforts conducted by Rabalais and co-workers are not adequate to characterize the annual maximum extent of hypoxia. They provide no information regarding phytoplankton, zooplankton and bacteria population dynamics during the critical late winter and spring months. Routine shelf-wide monitoring should be conducted every month of the year and with monitoring every two weeks during the critical months. In addition to having adequate modeling to characterize phytoplankton and zooplankton population dynamics and hypoxia, these monitoring programs should incorporate adequate data collection necessary to support required physical modeling. All data collection and laboratory research programs should be required to have Quality Assurance/ Quality control plans that meet the established requirements of EPA.

An adequate monitoring program in the Gulf would require significant additional financial resources and commitment of the various federal agencies. A sustainable level of effort on part of EPA would be required to ensure that research expenditures contributed to EPA program needs.

#### 5.1.2 Reevaluation of Nutrient Loads to the Gulf

The initial priority for river water quality studies should be toward understanding nutrient bio-availability in the lower basins and the Gulf. Proposals for large studies to evaluate the sources and fates of nitrogen in the mid and upper basins should receive a very low priority until it is determined that achievable nitrogen reductions would actually have a beneficial impact on Gulf hypoxia.

The nutrient data collected by the USGS for the lower Mississippi River has undergone considerable analysis for the CENR Reports. However much of this analysis was conducted under the theory that nitrate reduction held the most promise for mitigation of the Gulf hypoxia problem. All of the USGS data should be re-examined with equal attention to the possibility that phosphorus reductions could have a beneficial impact on Gulf hypoxia. In addition records held by other agencies should be examined. The many years of quality data obtained at the drinking water intakes at Jefferson Parish should receive special attention.

There should be a re-evaluation of the available nutrient data from the major point source NPDES discharges in the Mississippi and Atchafalaya Basins. Data deficiencies exist because many of these NPDES permits have no or inadequate monitoring and or reporting requirements. All the major NPDES permits discharge monitoring reports should be reevaluated to better characterize the amount of point source nutrients entering the Gulf system. Re-opening the permits and insertion of nutrient monitoring requirements in the re-issued permits necessary to collect data for developing effective nutrient strategies should be evaluated on a case-by-case basis.

# 5.2 Water Quality Modeling Improvement

## 5.2.1 Present Modeling Approach – A Simple Box Model

Gulf of Mexico water quality modeling presented in the CENR Report 1 (Sections 2.2.1-2.2.3.5, pages 5-15) refers to July and August data. The development of a simple box model of the eutrophication processes of the Louisiana Inner Shelf was part of the efforts to understand, predict and assess the influence of the Mississippi River nutrient impacts on the Gulf water quality and hypoxia. This model included steady state processes for salinity, phytoplankton, carbon, phosphorus, nitrogen, carbonaceous BOD and dissolved oxygen. The model used a coarse 21 grid representation of the inner shelf from the Mississippi River to the Louisiana Texas border. The sediment oxygen demand (SOD) and sediment nutrient fluxes are externally specified using observed data and model calibration. The model was calibrated using summer average conditions for 1985, 1988 and 1990. This simplified 21-segment steady state box modeling approach, calibrated to summer data, is inadequate to evaluate a complex system as the Gulf. Justic et al. (2002 and 2003) make extensive use of these simplified box models.

The assumption that the processes in the Gulf are steady state or can be represented by a steady state model is not reasonable. The comparison of the continuous records of the near bottom dissolved oxygen measured in the Inner Louisiana Shelf (Rabalais et al., 1994) indicates that there is considerable temporal variation in the dissolved oxygen concentrations in the bottom waters. Treating the SOD and sediment nutrient fluxes as constant boundary conditions limits the utility of the model for predictive purposes. Most likely the SOD and nutrient fluxes will vary seasonally with changes in flow and nutrient concentrations and will change in response to nutrient management controls.

An appropriate regulatory model must be developed for the Gulf on which to base very important funding decisions. Public funding should be dedicated for the support of adequate modeling efforts and other Gulf quality research.

#### 5.2.2 3 Dimensional Hydrodynamic and Water Quality Development

A 3 dimensional (3-D) hydrodynamic and water quality model must be developed for the "near shore" area or the inner shelf of the Gulf where the hypoxia problems occur and where the loadings from the rivers are delivered to the Gulf. Experienced 3-D hydrodynamic and water quality modelers must complete the model development, with oversight from EPA and/or other federal agencies modelers and in conjunction with the appropriate researchers. The water quality component must contain a full eutrophication component that would be able to determine and separate the effects of inputs of nitrogen, phosphorus, and carbon along with flow and other important chemical inputs, on the temporal and spatial extent of the hypoxia in the Louisiana Shelf. The model must also have a sediment nutrient flux and sediment diagenesis component. We also find that the physical processes in the Gulf were not adequately considered in the CENR reports or in the Box Model. The role of stratification was not adequately clarified and neither was the possible role of upwelling. DeMaster and Pope (1996) found that upwelling was a significant contributor to primary productivity in the waters of the Amazon Shelf. These processes can and should be incorporated in the 3-D modeling effort.

Recognizing the complexities of the Gulf's hydrodynamic, chemical and biological processes and the limited data available, the 3D model could be developed in phases, with the first phase concentrating on basic hydrodynamics, transport of the pollutant loads from the rivers and simple nutrient and phytoplankton processes. This would shed much more light on the limiting nutrient issue. As more research is completed and data are collected the model can be updated and refined.

The Navy has a hydrodynamic model for the entire Gulf of Mexico. The Navy model can be used to provide relevant information (surface water elevation, currents, vertical mixing coefficients, salinity and temperature) for use in the water quality model or can be used to develop hydrodynamic off shore boundary conditions for an independent 3-D hydrodynamic near shore model. An independent or separate hydrodynamic model may be needed for future predictive analyses. This issue needs further consideration. The Navy has been contacted and is willing to participate; funding would be needed for the computer and model processing time.

The Gulf water quality model must have a detailed eutrophication structure. The kinetic structure should include biochemical processes and rate equations which describe the interrelationships between phytoplankton biomasses, primary productivity, nutrients and nutrient cycling, carbon and dissolved oxygen. The model should calculate the time varying distribution of the various chemicals necessary to perform the phytoplankton and dissolved oxygen balance within the Inner Louisiana Shelf. The model must also contain a sediment nutrient recycling component which accounts for nitrogen, phosphorus, carbon, oxygen and other fluxes between the water column and the bottom sediments on the inner shelf.

Once the model has been calibrated with available data, the model can be used to evaluate the contribution of nitrogen, phosphorus and carbon to the spatial and temporal extent of hypoxia to the inner shelf. Once these interactions are understood and calibrated in the water quality model, then pollution reduction strategies can be developed that will lead to the minimization of the Gulf hypoxia problem.

## 5.2.3 Sediment-Water Column Exchange and Regeneration of N and P

One important aspect of nutrient dynamics and more specifically, meeting nutrient demands of primary producers, is the relative importance of sediment-water column exchange and regeneration of N and P (internal nutrient cycling). It is well known that there are significant differences between N and P recycling and hence re-supply rates within freshwater and marine ecosystems, especially shallow ones where sediment-water column exchange is greatly facilitated. This aspect of nutrient cycling dynamics (and controls on N and P availability) needs to be incorporated in the overall scheme of nutrient supply, availability and limitation. In

shallow systems like the Mississippi River plume and Northern Gulf of Mexico it is highly artificial to consider nutrient concentration and supply ratios based only on what is found in the water column at any point in time and space. N and P regeneration rates need to be established and incorporated into the overall nutrient cycling and availability schemes. This has not been adequately considered. This issue should be an essential component of any nutrient-productivity-hypoxia modeling effort.

#### 5.2.4 Impacts of Carbon on the Gulf Sediment Oxygen Demand

Recent study performed by researchers from University of Alabama (Carey et al, 1998) concludes that carbon inputs are a potentially significant contributor to the oxygen demand and therefore the hypoxia in the inner shelf. Similar results have been reported for the New York Harbor complex (St John et al, 1998), where 40 to 70 percent of the dissolved oxygen deficits in the western Long Island Sound and lower Hudson River could be caused by inputs of organic carbon. This carbon component must be included in the water quality model.

#### 5.3 Research Needs

#### 5.3.1 Light Limitation

During periods of maximum primary production, internal N and P cycling dynamics should be taken into consideration as these can affect and alter nutrient availability and limitation. Therefore, the additional issue of light limitation interacting with nutrient limitation in this region should be evaluated. How important light limitation is relative to P or N limitation on a seasonal basis appears yet to be resolved. Studies in other areas have indicated that algal blooms are occurring closer inshore in nutrient rich river plumes as sediment load and associated turbidity have decreased in the near-shore areas. Millions of acres of conventional row crop agriculture have been converted to no-till and conservation till in the Mississippi-Atchafalaya Basin. The millions of tons of reductions per year in soil loss may have already impacted phytoplankton population dynamics in the Gulf.

#### 5.3.2 Carbon Impacts to Hypoxia

The relative importance of phytoplankton production in the lower rivers as a source of carbon contributing to hypoxia does not appear to have been properly evaluated. If it is determined that carbon production in the rivers is making a significant contribution to hypoxia, a nutrient control strategy specific to the rivers may have to be developed and implemented.

While nitrate (NO3) may be the most important externally-loaded N source, it is by no means the only available N source, as N recycling in both the freshwater and marine portions of the Mississippi River plume, likely supply ammonium to phytoplankton as well. The relative impacts of nitrate and/or ammonium (or even organic N) on structuring phytoplankton communities need to be investigated as this can play an important role in establishing and promoting the types and fates of phytoplankton species and functional groups (i.e. diatoms, flagellates, cyanobacteria, dinoflagellates, etc.) supporting the base of the food web.

## 5.3.3 Bioavailability Studies on Nutrients

Comprehensive bioavailability studies on nutrients in the lower Mississippi and Atchafalaya Rivers should be conducted. The EPA published procedures for bioavailability studies (Algal Growth Potential) should be utilized. Nutrient addition protocols developed at the University of North Carolina by Dr. Hans Paerl and utilized in the Chesapeake Bay studies should be considered. At a minimum, monthly samples should be taken at St. Francisville, Belle Chasse, Venice and in the Gulf of Mexico off Southwest Pass. Enough additional stations should be established in the Gulf sufficient to resolve nutrient bioavailability issues. The studies in the Gulf

should be designed to build upon the information derived from the recently completed nutrient addition studies conducted by Dr. David Nelson and Dr. Quay Dortch.

Algal growth potential studies adequate to evaluate the sources and fates of bio-available nutrients should eventually be conducted in the mid and upper basins. When these studies are conducted, particular emphasis should be placed on the fate of dissolved inorganic phosphorus entering the rivers. There is a substantial body of literature that suggests that much of the dissolved inorganic phosphorus entering streams with high silt and clay content become bound to the sediment particles. Therefore, dissolved inorganic phosphorus entering the basin upstream may not be bioavailable when it enters the Gulf.

The extent to which bound phosphorus is regenerated/ recycled in the Gulf is apparently unknown. The very high DIN/DIP ratios reported in the high productivity portions of the plume by numerous researchers would suggest that bound phosphorus entering the Gulf from the rivers is probably not an important source of phosphorus for phytoplankton. However, this issue needs to be resolved.

#### 5.3.4 Denitrification in the Bottom Waters of the Gulf

The critical issue of denitrification under low oxygen conditions in the bottom waters of the Gulf needs substantial examination. Denitrification is apparently the mechanism responsible for the dissipation of very large quantities of nitrogen to the atmosphere. Denitrification may be an important factor in what appears to be an annual shift of substantial areas of the inshore northern Gulf from potential phosphorus limitation to potential nitrogen-phosphorus and nitrogen limitation.

## 5.3.5 Role of Nitrogen Fixation by Cyanobacteria in the Gulf

The role of nitrogen fixation by cyanobacteria in the Gulf needs substantial evaluation. If cyanobacteria produce nitrogen in sufficient quantities such that this nitrogen contributes to the production of substantial quantities of carbon that contributes to late season hypoxia, this would cast further doubt on the potential effectiveness of nitrogen reduction in the river basins. As referenced above, there is a substantial body of recent literature that suggests that nitrogen fixation is efficient enough to ensure that marine waters are never nitrogen limited when there is an adequate supply of available iron.

## 6 CONCLUSIONS

The Mississippi River provides water to the northern Gulf that is relatively rich in bio-available nitrate nitrogen relative to bio-available phosphate phosphorus. This excess nitrogen is evident in the high DIN:DIP elemental ratios observed, especially during the spring and early summer. These high elemental ratios are also evident in the low salinity water of the northern Gulf of Mexico. DIN:DIP ratios higher than 300:1 (Dr. Nelson, 2003, personal communication) can be observed in these lower salinity areas.

Sinking of phytoplankton and zooplankton fecal pellets is believed to be the source of organic matter in bottom waters. The decay of this material utilizes large quantities of dissolved oxygen and is believed to contribute to hypoxic conditions. There is a lack of compelling evidence that reduction of nitrogen would reduce the supply of organic matter fueling hypoxia.

Gulf of Mexico water quality modeling presented in the CENR Report 1 (Sections 2.2.1-2.2.3.5, pages 5-15) refers to July and August data. A number of years of Transect C data (Transect C data was collected monthly) were available prior to this modeling effort. Our analyses of the Transect C data lead us to conclude that July and August data is not representative of the nutrient ratios and primary productivity conditions during the part of the year for which there is highest primary production. Moreover, it is entirely plausible that the high primary

production during this period contributes significantly to the pool of organic matter that causes hypoxia. The exclusive use of July and August data from the northern Gulf to characterize conditions contributing to hypoxia provides an incomplete and distorted picture of the mechanisms regulating hypoxia. Basing hypoxia mitigation strategies on water quality predictions derived solely from conditions in July and August is inappropriate.

The observational evidence from the Mississippi River and the shelf waters of the Gulf of Mexico do not support arguments that a 30% reduction in total nitrogen would have an impact on hypoxia in the Gulf. In fact, our calculations suggest that nitrate reductions in the rivers in excess of 70% during the late winter and spring would be necessary to have any observable impact on primary production, and therefore, on hypoxia.

Additional research will be needed in order to improve the science necessary to understand the hypoxia issue adequately so as to adopt a hypoxia mitigation plan that has a reasonable chance of success. A better understanding of the sources and timing of the supply of organic matter fueling hypoxia is needed.

The CENR reports placed emphasis on levels of nitrogen reductions in the MRB and ARB, which cannot be supported by the available information. Also, the CENR reports failed to adequately consider the concept of "limiting nutrient". Even when the role of the limiting nutrient is correctly identified, this information has to be considered within the realm of technical and economic feasibility. EPA has often found that in aquatic systems where there is a great surplus of nitrogen, it is often more technically feasible and economically cost effective to drive the systems to severe phosphorus limitation.

Substantial evidence available at this time suggests that phosphate-phosphorus may have to be controlled in the MRB and ARB in order to have any measurable impact on primary production. Any nutrient reduction program implemented will have to be based on adequate science. However, economic studies will have to be conducted to ensure that the program is cost effective.

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